Temperature retrieval from stratospheric O3 and NO3 GOMOS data

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[1] The chemistry of some species is strongly dependent on temperature. The typical example is the nighttime NO_3 chemistry. We use a simple steady state relationship for NO_3 to derive temperature from measurements of O_3 and NO_3 by the satellite GOMOS (Global Ozone Monitoring by Occultation of Stars) instrument. GOMOS-retrieved temperatures are validated against ECMWF (European Centre for Medium range Weather Forecast) temperatures. The temperature between 30 and 40 km can be retrieved with a bias of 3°K and a precision of about 3°K. The small bias can easily be removed by slightly adjusting the temperature-dependency of the $NO_2 + O_3$ reaction in the steady state relationship. The results demonstrate that measurements of chemical species contain useful information on the temperature that can be extracted when the temperature-dependent chemistry is known accurately. This temperature-dependency of chemical systems could in the long term be exploited in weather data assimilation system. **Citation:** Marchand, M., S. Bekki, F. Lefèvre, and A. Hauchecorne (2007), Temperature retrieval from stratospheric O_3 and NO_3 GOMOS data, *Geophys. Res. Lett.*, *34*, L24809, doi:10.1029/2007GL030280.

1. Introduction

[2] The aim of data assimilation is to estimate the most probable state of the atmosphere based on an optimal combination of observational data and numerical model simulations. The application of data assimilation in the framework of atmospheric chemistry is still relatively new [*Lahoz et al.*, 2007]. Note that 'chemical' weather forecasting is now actively considered and even performed in several numerical weather prediction centres. The assimilation of data on chemistry could improve weather forecasting through various ways. For example, it has been shown that observational data on long-lived species (transport timescale $\ll$ chemistry timescales) such as ozone in the lower stratosphere contain useful information on winds and that their assimilation in dynamical models improve the quality of the wind fields [*Riishojgaard*, 1996; *Peuch et al.*, 2000]. Similarly, data on short-lived chemical species (chemistry timescale $\ll$ transport timescale) such as NO_x species could contain useful information on temperature. Indeed, the chemistry of some species is very strongly dependent on temperature. A typical example is the nighttime NO_3 chemistry. It is believed to be relatively simple in the stratosphere with three reactions [see *Marchand et al.*, 2004]. During the night, the temporal evolution of NO_3 species in the stratosphere is controlled by three reactions. NO_3 is produced by the reaction (R1) of NO_2 with O_3 and by the thermal decomposition of N_2O_5. The NO_3 sink is its reaction (R2) with NO_2 that produces N_2O_5. The NO_3 concentration is close to zero during the day because NO_3 is photolysed extremely quickly in the presence of sunlight. The rate constants of all three reactions are strongly dependent on temperature, making NO_3 concentration sensitive to temperature. This has been demonstrated by the very clear correlation found between satellite GOMOS measurements of nighttime NO_3 concentration in the upper stratosphere and temperature from ECMWF temperature [*Hauchecorne et al.*, 2005]. For a 1°K change, the NO_3 concentration changes by less than 10% typically. In the same way as the variability of chemical tracer species fields can provide information on winds, the variability of certain short-lived species could provide information on temperature. One possible application is the use of temperature as control variable in chemical data assimilation systems. Note that, up to now, the ability to extract temperature information from chemical measurements has not been demonstrated.

[3] The assimilation of short-lived chemical species is more challenging than the assimilation of chemical tracers because concentrations of short-lived species vary on timescales from less than a minute to one day, and hence detailed treatments of fast chemistry are required for simulating the variability. This added level of complexity partly explains why data assimilation systems for short-lived chemical species are less common than for chemical tracers. The objective of this paper is to test the ability to derive the temperature from NO_3 measurements whose nighttime chemistry is described above. Instead of using a full photochemical data assimilation system with temperature as a control variable, we consider regions where the NO_3 concentration can be described with a very simple steady state expression. In this configuration, temperature can be determined from NO_3 and O_3 measurements by adjusting the temperature in order to fit the calculated NO_3 to the measured NO_3. The paper is organised as follow. The second section describes briefly the GOMOS data, the steady state NO_3 expression and the temperature adjustment methodology. The final section presents and discusses the results.

2. GOMOS Data and Methodology

2.1. GOMOS Data

[4] The GOMOS instrument on board of the ENVISAT (Environment Satellite) satellite was launched by the European Space Agency on 1st March 2002. GOMOS is a UV-visible-near IR spectrometer on a sun-synchronous orbit observing stellar occultations [*Bertaux et al.*, 1991]. It provides 400 profiles per day all around the globe of O_3, NO_2, NO_3, H_2O, aerosols and Polar stratospheric Clouds

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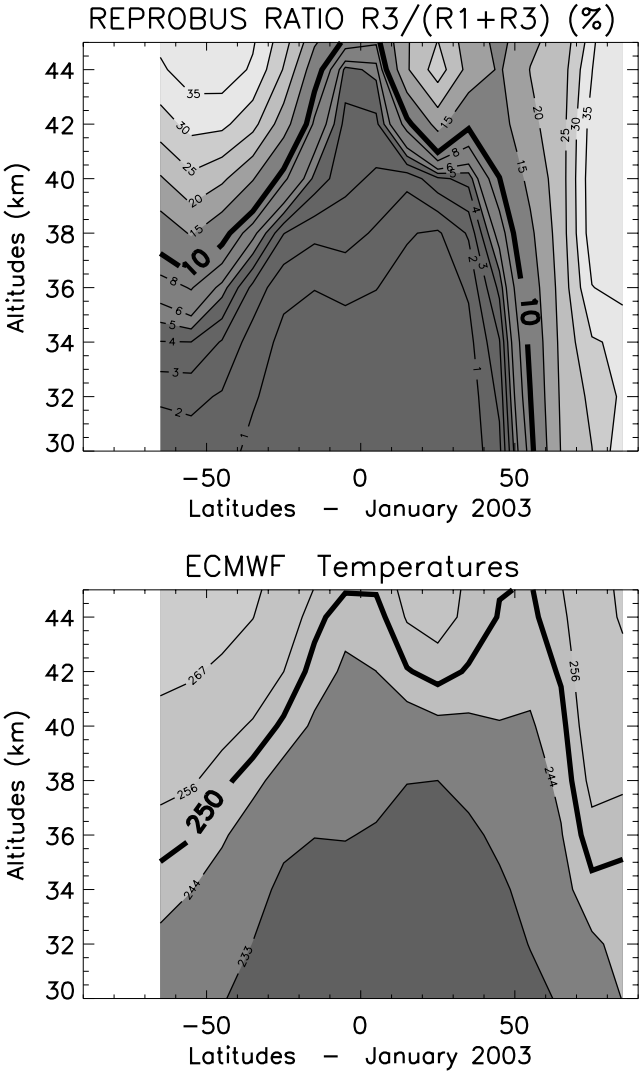

Figure 1. (top) Zonally-averaged contribution (in percent) of the N_2O_5 thermal decomposition to the NO_3 production (R3/R1 + R3) as a function of latitude and altitude for January 2003. (bottom) Zonally-averaged ECMWF temperature analysis.

(PSCs). Vertical profiles extend from 15 to 100 km for O_3 and from 20 to 50–60 km for the other constituents. All species are retrieved at the same time by a global least-square minimization of the mean difference between the measured transmission and the modelled transmission. A Tikhonov inversion technique with a second difference smoothness constraint [*Kyrölä et al.*, 1993] is applied in the version V6.0 of the data with a constant vertical resolution, fixed to 4 km in the case of NO_2 and for NO_3. The inversion is conducted globally. The retrieval algorithm for the data version (V6.0) is based on the use of differential absorption spectroscopy (DOAS). The vertical resolution in the region of interest is about 3 km for O_3 and 4 km for NO_3. The O_3 measurement errors are less than 3% typically. The NO_3 measurement total errors are highly variable, of the order of 130% when averaged globally. We only consider the most reliable GOMOS data. Therefore, only NO_3 measurements from bright stars with measurement errors of less than 15% are analysed here.

2.2. Nighttime NO_3 Steady State

[5] When the thermal decomposition of N_2O_5 (reaction R3) can be ignored, the steady state relationship for NO_3 is very simple [*Marchand et al.*, 2004],

$$[NO_3] = (k_1(T)/k_2(T)) \times ([O_3]/[M]) \quad (1)$$

with k_1 and k_2 being the rate constants of reactions (R1) and (R2) respectively and $[O_3]$ and $[M]$ being the concentration of O_3 and of air respectively. The strong temperature dependency of NO_3 originates from the rate constants ratio. The temperature is derived by minimizing a cost function of the misfit between GOMOS NO_3 measurement and NO_3 calculated from expression (1) with the control variable (i.e. variable adjusted during the minimization) being the temperature. The cost function is the difference to the square between GOMOS NO_3 and NO_3 calculated with relationship (1). In expression (1), the O_3 concentration is set to the value of the GOMOS O_3 measurement. The rate constants k_1(T)and k_2(T) and their temperature dependency are taken from the JPL recommendations [*Sander et al.*, 2003].

[6] The expression (1) is valid only when the thermal decomposition of N_2O_5 (reaction R3) can be ignored. In order to identify the best region where the expression (1) can be applied during the night (as GOMOS provides nighttime measurements), the chemical budget of NO_3 is calculated using numerical simulations from the chemistry-transport model REPROBUS (REactive PROcesses ruling the Ozone Budget in the Stratosphere) [*Lefèvre et al.*, 1994]. Figure 1 shows the nighttime contribution of the N_2O_5 thermal decomposition to the total NO_3 source, R3/(R1 + R3). The thermal decomposition of N_2O_5 is very sensitive to the temperature. As a result, the features seen in the R3/(R1 + R3) fields generally match those seen in the corresponding temperature fields as analyzed by ECMWF. The N_2O_5 thermal decomposition represents typically less than 10% of the total NO_3 source for temperature below 250°K. Nonetheless, there are regions where R3/(R1 + R3) does not correlate with temperature. In winter, R3/(R1 + R3) values range from 10 to 40% poleward of 55°N are not correlated to high temperatures. The (R3) channel is important at the winter pole because N_2O_5 concentrations are large. This enhancement of N_2O_5 concentration is due to the absence of photolysis during the polar night and to the polar descent that brings down higher concentrations of total nitrogen (NO_y). Overall, excluding from the polar winter regions and altitudes higher than 40 km, (R3) represents less than 10% typically of the total NO_3 source in the stratosphere. Therefore, we choose to apply the NO_3 steady state expression (1) in the region between 30 and 40 km and in the latitude band between 50°S and 50°N. There is a lower limit of 30 km because, below this altitude, the GOMOS measurements tend to have larger errors.

3. Results and Discussion

3.1. Case Study of Star 16, Antarès Alpha Scorpio

[7] We first present results for occultations of a bright star, the star number 16 (Antarès Alpha Scorpio) that provides among the best results. Figure 2a presents the temperature retrieved from GOMOS O_3 and NO_3 measure-

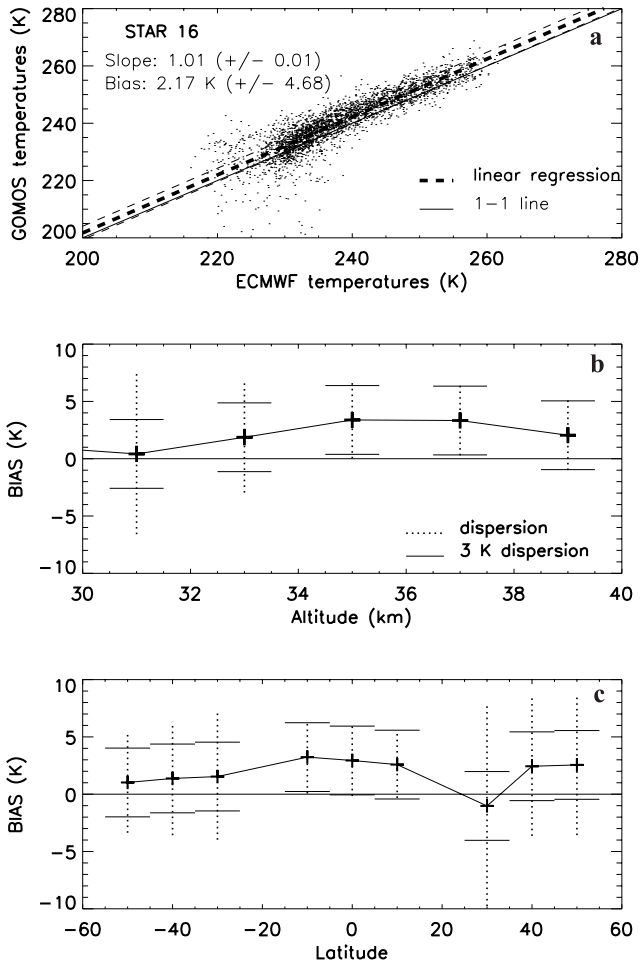

Figure 2. (a) Temperature retrieved from N_3 and O_3 GOMOS data (star number 16) as a function of the corresponding ECMWF temperatures. (b) Temperature bias ($T_{GOMOS} - T_{ECMWF}$, crosses) and dispersion (dashed vertical line) as a function of altitude. (c) Same as Figure 2b but as a function of latitude. For visual help, the 3°K dispersion is also indicated using horizontal lines.

ments as a function of the corresponding ECMWF temperature. The slope of the linear regression (dashed thick black line) on all the data points is 1.01 (±0.01) which is very close to unity, the 1–1 line (thin black line) slope. The difference ($T_{GOMOS} - T_{ECMWF}$) exhibits a small bias (i.e. systematic error) of 2.17°K with a standard deviation (i.e. random error), also called dispersion thereafter, of 4.68°K. There are some points that deviate very significantly from the 1–1 line below 235°K. These outliners often correspond to low NO_3 concentrations that can be found in the lowest part of the considered altitude region (30 to 40 km) and that are the more difficult to measure accurately with the GOMOS satellite instrument.

[8] The data points have also been binned according to their latitude and altitude. The binning resolution is 2 km in altitude and 10° in latitude. The results are displayed in Figures 2b and 2c; the bias (crosses) along with the dispersion (dashed vertical line) is plotted as a function of altitudes on Figure 2b and as a function of latitude on Figure 2c. For helping the visual comparison, the 3°K dispersion is also indicated with horizontal lines. The smallest values of dispersion are found above 33 km where, generally, the measurement errors are lower due to the higher NO_3 concentrations. If the data points at altitudes lower than 33 km are removed from the analysis, the global bias is slightly increased (2.81°K) but the dispersion is reduced by more than 1°K (3.43°K). The quality of the temperature determination and, in particular, the dispersion varies also with latitude (see Figure 2c). For a given star, measurement errors can depend on the latitude because the star occultation geometry (i.e. angle with the vertical of the star setting through the atmosphere) varies with latitude and can affect the quality of the NO_3 retrieval. For the star 16, although the bias is slightly larger in the tropics, the dispersion is up to a factor 2 lower there compared to temperature retrieval at middle latitudes.

3.2. Extension to Several Bright Stars

[9] The temperature has been retrieved for the measurements of the 20 brightest stars made between 33 and 40 km and between 50°S and 50°N. The bias varies little from one star to another, but not the dispersion that can exceed 10°K for certain stars. Random errors on temperature retrieval originate mostly from the random errors on NO_3 measurements. *Renard et al.* [2005] have shown that it is likely to be due to the combined effect of local fluctuations of NO_3 and temperature. This finding suggests that, on average, the GOMOS NO_3 measurement is relatively accurate (small systematic error) but its precision (random error) is strongly dependent on the star considered, even after filtering out the data using measurement errors provided by the GOMOS retrieval team. It is clear that our data filtering does not eliminate all the dubious data points. A proper estimation of satellite measurement errors and, in particular, the random component remains a difficult task.

[10] Among the 20 brightest stars, we select 4 stars (star number 1 (Sirius Alpha Canis Major), 2 (Canopus Alpha Carinae, 4 (Alpha Centauri) and 16 (Antarès Alpha Scorpio)) whose quality of NO_3 data is such that the temperature can be retrieved with a good precision (dispersion smaller than 3.5°K). These selected stars represent 4938 GOMOS data points and cover the globe from 50°S to 50°N during 2003. Averaged over all these stars, the bias and dispersion are found to be 2.67°K and 3.01°K respectively. Sensitivity tests show that the dispersion can be reduced further with a more stringent data filtering based on the value of the measurement error and the type of occultation geometry. However, whatever the additional data filtering, the bias does not change significantly and remains rather constant, around 3°K.

3.3. Minimization of Temperature Retrieval Bias

[11] There are a couple of potential sources of biases in the GOMOS temperature retrieval when using relationship (1). We ignore here possible biases in the ECMWF temperatures that are treated here as reference data. First, the steady state expression ignores the thermal decomposition of N_2O_5, resulting in NO_3 concentrations underestimated by about 5–10% typically over the considered domain. This translates in errors of about 2°K in the retrieved temperature. Second, NO_3 measurements by GOMOS can be subject to systematic errors. For example, although the

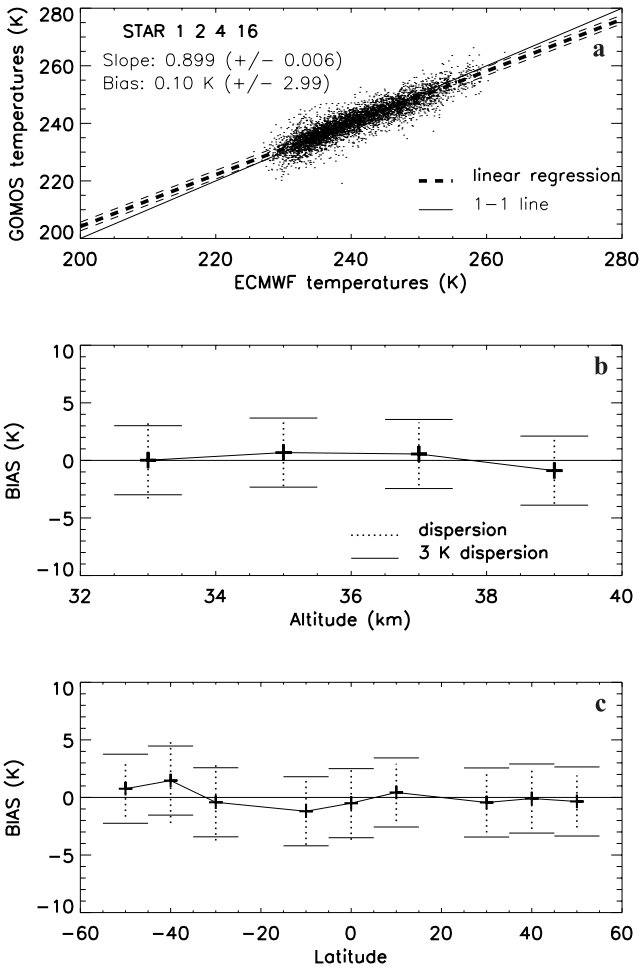

Figure 3. Same as Figure 2 but for all the data obtained with the selected stars 1, 2, 4, and 16 and after adjustment of the rate constant of reaction (R1).

shape of the NO_3 absorption cross sections is well known, uncertainties may pertain in their absolute values and their temperature dependence [*Renard et al.*, 2001; *Orphal et al.*, 2003]. Nonetheless, no very significant bias in GOMOS NO_3 measurements has been found in a previous validation study [*Marchand et al.*, 2004]. The errors on the O_3 measurements are ignored in our error analysis because they are negligible with respect to the errors on the NO_3 measurements. Third, there are uncertainties associated with the rate constants of $k_1(T)$ and $k_2(T)$ and their temperature dependency. Overall, the systematic errors on NO_3 measurements and the recommended reaction rate k_1 and k_2 values are estimated to result potentially in errors of up to 7°K in our temperature retrieval. This estimated temperature error originates mostly from the possible biases in k_1 and k_2 [*Toumi and Pyle*, 1992]. A way of minimizing the influence of these rate constant systematic errors on the temperature retrieval is described below.

[12] The uncertainties for $k_1(T)$ and $k_2(T)$ at 298°K have been estimated to be 15% and 20% respectively [*Sander et al.*, 2003]. The rate constant uncertainties are higher at the considered range of temperatures (220°K < T < 270°K) because of the uncertainties on the temperature dependencies of the rate constants. For a typical temperature of 240°K, we have estimated an uncertainties for k_1 and k_2 of about 30%. Several attempts have been made to estimate the rate constant of reaction (R1) from balloon-borne NO_3 measurements. *Renard et al.* [2001] found the best agreement between balloon-borne measurements carried out during the 90 s and photochemical model calculations for a value of 2430°K for the activation energy (E/R, which is strictly speaking the "activation temperature") of reaction (R1). They have updated this work using more recent balloon observations carried out between October 1998 and September 2002 [*Renard et al.*, 2005]. They found the best fit for $k_1 = 6.e - 13 \exp(-2740/T)$ that can be compared with the current JPL recommendation of $k_1 = 1.2e - 13 \exp(-2450/T)$ [*Sander et al.*, 2003]. We follow an approach similar to the *Renard et al.* [2005] work. For all the data from 4 selected stars, we minimize simultaneously the difference to the square between measured and NO_3 calculated from (1) using ECMWF temperature; the variables adjusted during the minimization are the rate constant parameters (pre- exponential factors, temperature dependencies) of (R1) and (R2). This procedure does not imply that the rate constants are necessary biased because there are other possible sources of biases in the system. This procedure is just a convenient way of removing a large part of the bias in our retrieved temperature. A quasi- newtonian minimization technique is applied taking the JPL recommendations as initial values. Figure 3 presents the results after adjustment. The global bias becomes almost negligible at 0.1°K (±2.99°K). The activation energy of (R1) is the only parameter affected by the minimization. It is not totally surprising because (R1) is the more sensitive to the temperature than (R2). After adjustment, the new activation energy of (R1) is found to be equal to 2400°K. The difference between $k_1(T)$ calculated with the value of 2400°K and $k_1(T)$ calculated using the JPL recommended value (2450°K) is 23% which is within the JPL recommended uncertainties for $k_1(T)$ (30%). The new activation energy is still very close to the value of 2430°K derived by *Renard et al.* [2001] but it is about 10% lower than the value of 2740°K found by *Renard et al.* [2005] study. Note that, the comparison with this latter study is not as straightforward because their adjustment also led to a factor 4 enhancement of the pre-exponential factor of k_1 that is also called the Arrhenius A-factor. Overall, the results demonstrate that measurements of chemical species contain useful information on the temperature that can be extracted when the temperature-dependent chemistry is known quantitatively. Another good example of temperature-dependent chemistry is the nighttime decay of NO_2 that is controlled by reaction (R1) [*Marchand et al.*, 2003]. Note that this type of study represents also a good way of testing chemical reaction temperature-dependencies determined in laboratory. This temperature-dependency property of certain atmospheric chemical systems could in the long term be exploited in weather forecasting with the use of temperature as a control variable in chemical data assimilation system.

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